

Evaluation of thiol-modified vermiculite for removal of Hg(II) from aqueous solutions

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Introduction

The intense industrial activities lead to a significant increase in the loading of potentially toxic compounds such as Hg(II) species in the environment. Among methods for removal of Hg(II) from aqueous media, adsorption on clay minerals is the cheapest and the easiest to operate¹ due to their abundance in environment and low cost. These minerals can be subjected to chemical modification to enhance their affinity towards an adsorbate or class of adsorbates. The reactive groups in vermiculite and the exchangeable interlamellar cations enable chemical modification for introduction thiol groups in the structure, enhancing the affinity of the material by Hg(II)². In this work, the adsorption of Hg(II) on Na⁺-homoinic vermiculite (Na-VT) was compared with the material organofunctionalized with cysteine (CYS-VT), cysteamine hydrochloride (CTA-VT) and 3-mercaptopropyltrimethoxysilane (3MPS-VT) in different conditions of pH and ionic strength. The determination of Hg(II) was made by chronopotentiometry mechanized by sequential injection analysis (SIA).

Results and Discussion

The cation exchange capacity (CEC) of Na-VT was $1.154 \pm 0.006 \text{ mmol g}^{-1}$. A rapid kinetics of interaction between Hg(II) and the different materials was observed; 60 min of contact time were suitable for adsorption and to avoid the complexation with the MES buffer. An increase in percent removal of Hg(II) with the increase in adsorbent dosage (25 mg to 100 mg) was observed for CTA-VT and 3MPS-VT (67.0 to 89.7 %, and 58.0 to 99.7 %, respectively) due to the increased amount active sites available. Contrary, only small increase was observed for Na-VT and 3MPS-VT (55.5 to 64.1 %, and 58.1 to 68.5 %, respectively) with the increase of adsorbent dosage. CTA-VT shows the higher adsorption capacity parameters of Langmuir and Freundlich equations ($q_{max} = 41 \pm 5 \text{ } \mu\text{mol g}^{-1}$ and $K_f = 13 \pm 1 \text{ } \mu\text{mol}^{-1/n} \text{ g}^{-1} \text{ L}^{1/n}$). The $1/n$ (1.1 ± 0.02) parameter of the Freundlich equation suggests that binding of Hg(II) to CTA-VT occurs predominantly at sites of homogeneous adsorption energy. CYS-VT had also

an increase in the adsorption capacity, but this effect is noticed only for the higher loadings of Hg(II) of the adsorption isotherm. The main alteration of Na-VT after 3-MPS modification was the increase in heterogeneity of binding sites, due the presence of silanol and aluminol groups, and the introduced thiols. Modification of Na-VT with 3-MPS didn't increase significantly the adsorption capacity. The silylation reaction of the silanol and aluminol groups obey either 1:1 or 1:2 stoichiometries, that is, one or two of these groups are modified to afford one other group containing a thiol functionality. Assuming that all the carbon content in the modified Na-VT comes from the thiols, and that binding of Hg(II) by the modified vermiculites obeys a 1:1 stoichiometry, the q_{max} values correspond to 15.2, 35.5 and 58.7 % of the total content of thiol groups in CYS-VT, CTA-VT and 3-MPS-VT, respectively.

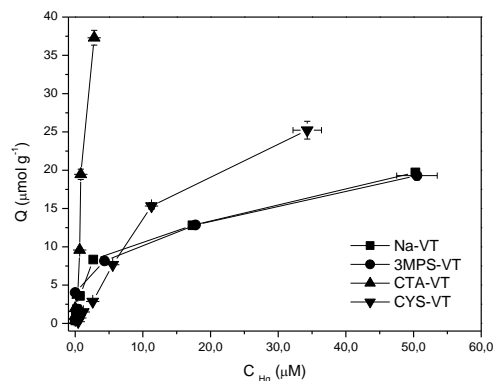


Figure 1. Adsorption isotherms ($25.0 \pm 0.5 \text{ } ^\circ\text{C}$) of Hg(II) on Na-VT, CYS-VT, CTA-VT and 3-MPS-VT in $0.05 \text{ mol L}^{-1} \text{ NaNO}_3$ at $\text{pH } 6.0 \pm 0.1$ (0.01 mol L^{-1} MES buffer).

Conclusions

All materials have a potential for application in the removal of Hg(II) in aqueous media, especially the modification with CTA, the best adsorbent in terms of capacity and energy of interaction with Hg(II) among the materials studied.

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